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RESEARCH MEMORANDUM

DEVELOPMENT OF METAL-BONDING ADHESIVE FPL-710 WITH IMPROVED HEAT-RESISTANT PROPERTIES

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Forest Products Laboratory

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DEVELOPMENT OF METAL-BONDING ADHESIVE FPL-710 WITH IMPROVED HEAT-RESISTANT PROPERTIES

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SUMMARY

An adhesive, FPL-710, has been developed that produces higher strength at temperatures up to 600° F than heretofore obtained and possess good resistance to aging at temperatures as high as 450° F. The adhesive also has acceptable resistance to creep and to immersion in various organic solvents. The preparation and recommended bonding procedures are described herein. The principal limitations of adhesive FPL-710 are that it is somewhat brittle and possesses marginal bend and fatigue strength and, presumably, low peel strength.

INTRODUCTION

An earlier study of the performance of various commercial adhesives in aluminum-to-aluminum lap joints at temperatures from -70° to 600° F indicated that the currently available adhesives were generally unsuitable for service at temperatures of 450° F or higher and a number were significantly affected by temperatures from 250° to 450° F (reference 1). It was evident from this evaluation of commercial adhesives that if metal-bonding adhesives were to meet the projected requirements of the aircraft designer for use in certain aircraft parts, particularly in the newer, high-speed aircraft and missiles, it would be necessary to develop adhesives with improved heat-resistant properties.

A research study was accordingly undertaken at the Forest Products Laboratory under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics to develop an adhesive suitable for bonding metal to metal for use in aircraft that would possess improved strength properties at elevated temperatures and improved resistance to continuous exposure at elevated temperatures.

An adhesive, FPL-710, has been developed that produces higher strength at temperatures up to 600° F than heretofore obtained and possesses good resistance to aging at temperatures as high as 450° F. The adhesive also has acceptable resistance to creep and to immersion in various organic solvents. The principal limitations of adhesive FPL-710 are that it is somewhat brittle and possesses marginal bend and fatigue strength and presumably low peel strength, but further development work is being continued to improve these characteristics.

EXPERIMENTAL PROCEDURE

Preparation of Adhesive FPL-710

Adhesive FPL-710 is a heat-activated thermosetting mixture of a commercially available phenol-formaldehyde resin and a commercially available epoxy resin, with a curing agent dissolved in methyl ethyl ketone to give a composition with a solids content of about 57 percent.

A method for the preparation of FPL-710, which has developed satisfactory bonds in laboratory tests, is given below. The formula is:

Bakelite BV 9700[a], grams	100
Epon resin 1007[b], grams	20
Methyl ethyl ketone, grams	20
Hexamethylenetetramine, U.S.P., grams	6

(a) The Epon resin 1007 is dissolved in the methyl ethyl ketone.

(b) The Bakelite BV 9700 is supplied in solution. The solutions of Bakelite BV 9700 and Epon 1007 and hexamethylenetetramine are mixed together and refluxed for 15 minutes with constant stirring. The mixture is then cooled and may be stored in a closed container at room temperature for a period of 3 months or at 40° F for over a year.

(c) Just prior to use as an adhesive, the FPL-710, as prepared above, should be thinned with 15 parts by weight of methyl ethyl ketone for each 10 parts of adhesive solution.

Recommended Application and Bonding Procedure

The following steps in bonding are presently recommended for most consistent results with FPL-710:

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[a]Supplied by Bakelite Corp.
[b]Supplied by Shell Chemical Corp.

(1) Clean the aluminum surfaces by immersion for 5 to 10 minutes in a solution of sulfuric acid (10 grams) and sodium dichromate (1 gram) in 30 grams of water at 140° to 160° F and follow with a rinse in cold running water and then hot running water or steam.

(2) Thin 10 parts by weight of the adhesive with 15 parts by weight of methyl ethyl ketone and use the thinned solution within 24 hours.

(3) Apply one brush coat to each surface to be bonded with a minimum of brushing to prevent formations of bubbles. A dry film thickness of about 0.001 inch is recommended.

(4) Air-dry the adhesive film for at least 2 hours at room temperature; then precure for 15 to 20 minutes in an oven at 180° F with adequate air circulation and sufficient heat capacity to heat the metal to within 5° F of the precure temperature in 10 minutes.

(5) Assemble the parts to be bonded and press at 280° F for 1 hour at a pressure of 50 psi or higher.

The adhesive may be removed from brushes and containers with a mixture of acetone and cellosolve.

Test Methods and Test Results

Test specimens of 0.064-inch clad 24S-T3 aluminum alloy with a 0.5-inch lap joint, as described in reference 2, were used for the evaluation of shear strength in tests made immediately at each of the test temperatures and after the various aging conditions, immersion tests, and long-time loading tests. The same specimens were used in the bend tests. Specimens with a 0.375-inch lap joint, also described in reference 2, were used in fatigue tests. Tension tests were made on two 1-inch aluminum cubes bonded together. After bonding, the bond area was reduced to 0.25 square inch by notching at the glue line to prevent excessive distortion of the cube or shearing of the pins in the holding-jig assembly.

Lap shear and tension test specimens were loaded in self-alining grips at the rate of 300 pounds per 0.5 square inch per minute. Bend test specimens were loaded flatwise at the center as a simple beam with a 1.5-inch span at the rate of 200 pounds per minute. The loading block was over the center of the bonded area.

Axial-loading fatigue tests were made with the specimens (0.375-in. lap joints) stressed primarily in shear by tension loading. The stress ratio (minimum repeated load for each cycle divided by maximum repeated load for each cycle) was 0.10 for all fatigue tests. The number of cycles to failure was determined for each specimen loaded at different levels to produce failures in the range from 5000 to 10 million cycles. The stresses are normally plotted against the number of cycles to failure (S-N curves). In compliance with reference 2, the fatigue strength is considered as the load that causes failure at 10 million cycles as determined from the S-N curve.

The temperature in tests at elevated temperature and during aging was controlled to within ±3° F of the desired temperature. When testing at elevated temperature, a period of 3 to 5 minutes was required to heat the specimen from room temperature to the test temperature. In tests made immediately at the elevated temperature (table 1), the load was applied as soon as the temperature of the specimen reached the desired temperature. In tests according to reference 2 (table 2) the specimen was heated for 30 minutes before the load was applied.

SUMMARY OF RESULTS

In previous studies, various resin and adhesive-type materials were evaluated as components for adhesives by noting their adhesion to aluminum, the strength of the adhesive bond when tested at room temperature and at elevated temperatures (usually 450° F), and the resistance of the bond to thermal degradation when exposed continuously for 192 hours at an elevated temperature (450° F). The materials included in the evaluation were phenol-formaldehyde, melamine-formaldehyde, polyester, silicone, polyamide, buna-N rubber, polyacrylates, copolymers of acrylates, and various epoxy resins. Of these materials, adhesive formulations employing certain phenol resins in combination with buna-N rubber, polyacrylates, copolymers of acrylates, and certain epoxy resins were considered promising. The most promising of these adhesive formulations were those employing phenol resins and epoxy resins, and subsequent work has been done on the further development of these particular formulations into an improved heat-resistant adhesive.

The present most promising adhesive formulation, designated as FPL-710 and described in this report, is composed of phenol and epoxy resins with certain modifications to improve the strength of the adhesive bond at elevated temperatures and to improve the resistance of the adhesive to thermal degradation. An important finding in the work to date has been the importance of the control of conditions in the bonding process in determining ultimate performance of the bonded joints at temperatures of 450° F or higher. In particular, it appears that control of the amount and method of adhesive application and the air-drying and precuring conditions before pressing are important in controlling the amount of solvent and other volatiles retained in the joint, since residual solvent apparently has a degrading effect on the adhesive bond at elevated temperatures.

Strength Properties of FPL-710 Bond

A summary of the strength properties of the FPL-710 bonds of aluminum to aluminum, when cured at 320° F, is presented in table 2. The adhesive appears to meet the requirements of reference 2 for those conditions evaluated, except for lap shear strength at -70° F, bend strength at room temperature, and the fatigue requirements at room temperature. Fatigue performance at -65° to -70° F was not investigated. The adhesive presumably possesses low peel strength. Recent work has indicated that curing the bonds more slowly at 280° F instead of at 320° F resulted in higher bend strength values meeting the requirement of 150 pounds in preliminary tests.

Adhesive FPL-710 gives particularly promising results at elevated temperatures where it far exceeds the specification requirements for shear strength at 180° F and has developed an average strength of about 1200 psi at 450° F. Results as high as 1900 psi have been obtained at 450° F in some tests. The reason for this variation is not as yet known. Further heat and aging tests are discussed later. Metal bonds tested after immersion in water, ethylene glycol, hydrocarbon fluid, and isopropyl alcohol easily met the specification requirements. FPL-710 adhesive also developed a high tension strength at temperatures ranging from -70° to 180° F when tested between two aluminum cubes.

Heating and Aging Resistance of FPL-710 Bonds

The performance of FPL-710 and several other commercial adhesives in lap-joint specimens of clad 24S-T3 aluminum alloy are compared in table 1. The commercial adhesives listed include those with highest performance at elevated temperatures in the earlier evaluation work (see reference 1).

Lap joints bonded with FPL-710 developed relatively high strength when tested immediately at temperatures up to 600° F and were very significantly better than all other adhesives when tested immediately at this temperature. Joints properly made with FPL-710 have also shown a high degree of resistance to thermal degradation as indicated by the retentions of joint strength at temperatures up to 450° F after aging for 192 hours at these elevated temperatures. Test specimens aged for 192 hours at 450° F and subsequently tested at room temperature retained about half their initial strength at room temperature but still had a strength exceeding 1200 psi and were approximately equal in strength to joints tested at 450° F after 192 hours at this temperature.

The test results on FPL-710 adhesive shown in table 1 were obtained on bonds that were cured at 320° F for 30 minutes at 50 psi. A curing period of 1 hour at 280° F is now believed to produce bonds of improved properties, but test results at all test conditions, with this lower curing temperature, are not yet available.

The outstanding commercial adhesives, with respect to strength at elevated temperatures and resistance to aging at elevated temperature, were adhesives F, G, and H. Adhesive FPL-710 was superior to these adhesives in the strength of joints tested immediately at the elevated temperatures, particularly at temperatures of 450° and 600° F. Exposure of the bonded joints made with adhesives F, G, and H for 192 hours at either 350° or 450° F resulted in higher joint strength when subsequently tested at the elevated temperatures than when tested immediately at these temperatures.

Joints made with adhesive FPL-710 showed a marked increase in strength when tested at 350° F after aging 192 hours at that temperature, compared with those tested immediately at 350° F, and only a slight increase in strength at 450° F as a result of the 192-hour aging at this temperature. Joint strength values of 1000 psi or higher in tests made immediately at 450° F have been obtained consistently with numerous different batches of FPL-710. Reproducible high-quality joints at 600° F are more difficult to obtain. Only a limited investigation has been made of factors that influence the strength and aging properties of the adhesive at 600° F, but these preliminary tests have shown that close control of solvent removal and bonding conditions are required to obtain optimum performance.

Variables Affecting Bond Strength of FPL-710

The following observations on the effects of variations in formula and bonding conditions on the bond strength of FPL-710 are based on a considerable volume of test data accumulated during the progress of the development of the adhesive:

1. Refluxing of the resin solutions of Bakelite BV 9700 and Epon 1007 with hexamethylenetetramine for at least 5 minutes was important in the subsequent development of acceptable bond strengths.

2. Application of the adhesive FPL-710 on the metal to be bonded without thinning with methyl ethyl ketone resulted in inferior bonds. Thinning 10 parts by weight of adhesive with 15 parts of methyl ethyl

ketone produced bonds of highest quality. A dry film thickness of about 0.001 inch of adhesive on each surface to be bonded seems to give optimum results.

3. The thinned solution of adhesive should be used on the day of thinning.

4. The high joint-strength values presently reported were obtained when aluminum surfaces were cleaned by a process using sulfuric acid and sodium dichromate. Other simpler methods of cleaning the aluminum are now being investigated.

5. Control of precure conditions and removal of solvent before bonding are important considerations in the development of optimum strength at elevated temperatures and resistance of adhesive to thermal degradation at elevated temperature.

6. Lap-joint shear strength at room temperature was higher when joints were cured at 280° F than when joints were cured at 320° F.

7. Bend strength was improved when joints were cured at 280° F instead of 320° F and when the bonding pressure was 50 psi or higher.

8. The thickness of clad aluminum alloy used in the lap-joint shear specimen affected the strength of the adhesive bond at 600° F; lap joints of 0.032-inch clad aluminum alloy were appreciably lower in strength than joints of 0.064-inch clad aluminum alloy.

9. Lap joints of stainless steel bonded with FPL-710 were approximately 1000 psi lower in strength at room temperature but about 200 psi higher in strength at 600° F than lap joints of 0.064-inch clad aluminum alloy.

Forest Products Laboratory
Madison, Wisc., June 13, 1952

REFERENCES

1. Eickner, H. W., Olson, W. Z., and Blomquist, R. F.: Effect of Temperatures from -70° F to 600° F on Bond Strength of Lap Shear Specimens of Clad 24S-T3 Aluminum Alloy and of Cotton- and Glass-Fabric Plastic Laminates. NACA TN 2717, 1952.

2. U. S. Air Force: Adhesive, Metal to Metal, Structural. Spec. No. 14164, U. S. Air Force, Sept. 20, 1949.

TABLE 1.- RESULTS OF TESTS MADE AT VARIOUS TEMPERATURES ON CLAD 24S-T3 ALUMINUM ALLOY LAP SHEAR SPECIMENS BONDED WITH FPL-710 AND EIGHT COMMERCIAL ADHESIVES

[Test values were obtained on a 0.5-inch lap-joint specimen and then doubled to convert to shear strength on a basis of psi. Each value is average of results of tests on five or more specimens, except for test 3, in which two specimens were tested for each value with commercial adhesives.]

Adhesive (1)	Test 1: Specimens tested immediately after reaching - (2)																	
	-70° F		80° F		160° F		180° F		200° F		250° F		350° F		450° F		600° F	
	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)
FPL-710	1882	77	2664	16	----	—	3136	16	----	--	----	--	1312	14	1212	21	920	0
A	5626	100	3060	57	2010	76	----	--	1854	32	1660	42	1306	22	950	35	66	100
B	1660	100	4164	48	1788	12	----	--	2360	7	186	0	32	0	20	0	24	0
C	3464	3	3878	23	2206	17	----	--	1246	14	500	0	258	0	100	0	64	0
D	----	---	3164	44	----	--	----	--	1458	53	----	--	----	--	----	--	---	---
E	----	---	4594	4	----	--	----	--	3846	57	----	--	----	--	----	--	---	---
F	3266	94	3512	11	2040	12	----	--	1512	14	1332	8	924	29	538	76	228	86
G	1204	99	4834	1	----	--	2230	19	----	--	1564	14	938	17	518	27	210	12
H	2980	86	2838	5	----	--	1326	0	----	--	----	--	----	--	264	0	---	---

Adhesive (1)	Test 2: Specimens tested at temperatures shown below after 192 hr at such temperatures								Test 3: Specimens tested at 80° F after exposure for 192 hr at -							
	160° F		250° F		350° F		450° F		160° F		250° F		350° F		450° F	
	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)	Average shear strength (psi)	Adhesion failure (percent)
FPL-710	----	--	----	—	2972	8	1318	18	----	—	----	--	2266	11	1268	8
A	2024	65	1364	16	1114	97	0	100	2472	5	1566	85	1408	100	0	100
B	2488	4	1838	10	640	9	92	0	4310	40	4750	20	2510	10	230	0
C	3158	10	1858	0	574	0	322	0	3070	28	3030	90	2570	52	1216	8
D	----	--	----	--	----	--	0	93	----	--	----	--	----	--	0	----
E	----	--	----	--	----	--	210	7	----	--	----	--	----	--	0	---
F	2414	10	2012	24	1482	93	972	89	3792	10	3358	42	2958	94	1212	89
G	----	--	2867	8	2339	14	1252	97	----	—	4719	7	3943	7	1413	31
H	----	--	----	—	----	--	1030	11	----	--	----	--	----	--	----	---

[1] Data reported for adhesive G are from tests conducted under a project in cooperation with Air Force's Wright Air Development Center. Those for adhesive H are from a project conducted in cooperation with ANC-23 Panel on Aircraft Design Criteria. The data on all other commercial adhesives are from reference 1.

[2] Specimens were tested immediately after the glue line reached the temperature indicated. This usually required from 3 to 5 minutes in the test chamber after the specimen was inserted.

TABLE 2.- AVERAGE STRENGTH PROPERTIES OF

ADHESIVE FPL-710 IN VARIOUS TESTS

[Tests conducted according to reference 2. Each value is average of results of tests on at least five test specimens. All tests except fatigue strength and tension cube were made on lap shear specimens of 0.064-in. clad 24S-T3 aluminum alloy with a 0.5-in. lap joint. Fatigue specimens had a 0.375-in. lap joint. Tension cubes were two 1-in. aluminum cubes, reduced in the bonded joint to 0.25 sq in.]

Test temperature (°F)	Type of test	Strength requirements of reference 2 (psi)	Strength values of [a]FPL-710 (psi)
-65 to -70	Shear strength	2500	1950
72 to 76	-----------do------------	2500	2774
180	-----------do------------	1250	2970
450	-----------do------------	--------	1212
72 to 76	30-day immersion in water	2000	3072
72 to 76	7-day immersion in ethylene glycol	2000	2712
72 to 76	7-day immersion in hydrocarbon fluid	2000	2866
72 to 76	7-day immersion in isopropyl alcohol	2000	2784
72 to 76	Long-time strength	1600	1600 or higher
180	-----------do------------	800	900
72 to 76	Bend	150 (lb)	117 to 132 (lb)
72 to 76	Fatigue strength	650	500
-65 to -70	Tension cube	--------	5929
72 to 76	-----------do------------	--------	8149
180	-----------do------------	--------	6589

[a]Bonding conditions: The metal was cleaned in a solution of sulfuric acid and sodium dichromate. The adhesive was thinned with 50 percent by weight of methyl ethyl ketone. One coat was applied by brush to each surface; the specimens were air-dried overnight at 80° F, precured for 10 min at 200° F, and pressed at 320° F for 30 min at 50 psi.

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